

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in and relating to Modified Aminotriazine-Formaldehyde Resin Compositions

We, BRITISH INDUSTRIAL PLASTICS LIMITED, a Company organised under the Laws of Great Britain, Haymarket House, Haymarket, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

10 This invention relates to thermosetting compositions and more particularly to the manufacture of improved thermosetting compositions comprising aminotriazine-aldehyde resins, especially such compositions as are used as thermosetting moulding and laminating compositions, and mouldings and laminates produced therefrom.

15 According to the invention thermosetting compositions comprising aminotriazine-aldehyde resins are modified to improve their plasticity or flow and fusibility characteristics under heat by the incorporation in the composition of one or more polyethylene glycols of the typical composition

20 $\text{HO}(\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$, and of molecular weight within the range 722 to 7542, i.e. where $n=15$ to 170. Such compositions containing a partially-condensed aminotriazine-aldehyde resin and a suitable

25 polyethylene glycol are particularly advantageous, and it is possible, according to the invention, to provide cured, moulded and laminated articles by forming such a partially-condensed compositions and then curing.

30 In the manufacture of modified or plasticised compositions according to the invention, formaldehyde is the preferred aldehyde but other aldehydes, e.g. benzaldehyde, may be used as well, or instead, if desired.

35 The preferred aminotriazine is melamine, but related compounds such as ammeline, melam and benzoguanamine may be used as well, or

instead, if desired. The ratio of aldehyde to aminotriazine generally ranges from 0.43 to 2—CHO radicals per —NH₂ radical of the aminotriazine employed. Thus, in the case of melamine formaldehyde resins molecular proportions of 1:3:1 to 6:1 of formaldehyde to melamine may be used, which corresponds to 0.43 to 2—CHO radicals per —NH₂ radical of the melamine used. In the case of melamine a mol ratio of 1.5:1 to 3:1 is preferred. It will be understood that suitable resin-forming reagents may be employed as well as, or instead of the resins themselves.

40 The preferred proportions of polyethylene glycol will normally range for most purposes from 2% to 30% by weight on the weight of aminotriazine-aldehyde resin or resin-forming reagents used, but the invention is not restricted or limited to these proportions. The polyethylene glycols may be added if desired as reagents or modifiers in the initial condensation process to form the aminotriazine-aldehyde resin, or at any convenient stage after partial condensation, and submitted thereafter to further condensation or final curing, whenever desired. Catalysts and/or initiation agents, and other additives may be added if desired.

45 If desired, the aminotriazine-aldehyde components of such systems may comprise alkylated or partially alkylated products resulting from the reaction of the aminotriazine and aldehyde with alcohols, preferably monohydric alcohols, containing 1—3 carbon atoms, such as methyl or ethyl alcohol, and co-reaction of the amino resin with the polyethylene glycol may be carried out simultaneously in the presence of one or more alcohols if desired. Alternatively, the reaction with an alcohol may be carried out after partial condensation has taken place.

50 Suitable polyethylene glycols over the

(Price)

desired range of molecular weights are available commercially. Minor amounts of higher or lower molecular weight glycols may be present as well, if desired, but in general it is found that resin-compatibility diminishes progressively with increasing molecular weight; and water solubility, which tends to impair water-resistance of the cured resin products, increases with lower molecular weight, thus limiting the usefulness of materials outside the above defined range.

Suitable materials are "Carbowax" (Registered Trade Mark). Polyethylene glycols 1000 (mol wt. range 950—1050); 1540 (mol wt. range 1300—1600); 4000 (mol wt. range 3000—3700); and from another source (Oxitane Ltd.) technical grades described as 800 (mol wt. range 760—840); 1000 (mol wt. range 950—1050); 20 1500 (mol wt. range 1300—1600); 4000 (mol wt. range 3000—4000); 6000 (mol wt. range 5000—7500).

When present during the condensation reactions, the polyethylene glycols appear to react as resin-modifiers and contribute appreciably to improved storage stability of the aqueous resin compositions. They may be added, alternatively, to pre-condensed resin compositions solutions or dispersions which may then be dried and heat-treated, or if desired solid fusible resin compositions or partially-condensed dry powder resin compositions may be blended with the polyglycols and heat-treated, to advance the degree of polymerisation while conserving adequate fusibility of the products.

It is possible thereby to obtain partially-cured resin products which even after very thorough pre-drying or pre-cure still retain adequate resin-flow and fusibility for hot-press moulding and laminating applications. The resultant cured products accordingly have much improved dimensional stability (mould-shrinkage and after shrinkage are reduced), better resistance to crazing under dry heat and much superior electrical properties.

Hot-pressed products of the invention generally have improved plasticity and flexibility, especially while hot or when reheated. Machining properties of products comprising cellulose or other organic fillers, especially hot punching and post-forming properties, are thereby improved.

55 The modified resins are especially valuable for the production of glass-fabric laminates for high-duty electrical insulation, where previously no really suitable resin plasticisers or modifiers for aqueous systems of amino-triazine-aldehyde resins have been found to give all the requirements of high dielectric strength, good water-resistance, low power factor at 90° C., good resistance to tracking and arcing, and non-inflammability of the finished products.

Melamine-resin bonded glass fabric laminates for electrical insulation are normally made by impregnating electrical-grade glass fabric with an aqueous solution of the resin and drying the stock in a current of hot air until all the free water is evaporated and the resin has been advanced in condensation to some extent by partial pre-cure, resulting in some further degree of dehydration. The resin-loaded fabric is then cut into sheets and a plurality of these plies is then consolidated and cured in a hot-press. For good consolidation it is essential that the resin shall have adequate flow and fusibility to allow complete expression of air so that all voids are filled with resin and so eliminated; and for good electrical insulation values it appears essential that the residual hydroxyl-content, or methylol groups, of the resin shall be reduced by drying and pre-cure to the lowest possible value consistent with retention of sufficient resin fusibility, so that further elimination of water from the resin during cure in the hot-press is also reduced to a minimum. With unmodified resins obtained by the aqueous condensation of melamine and formaldehyde it is found, because of these considerations, that although laminates of high dielectric strength can be made without any great difficulty, the residual traces of water of condensation liberated during cure of the resin in hot-pressing are contained in the products, and their effect is to cause a very considerable worsening of the power factor of the material in use at elevated temperatures. A further defect is that under dry heat such products are found to be very prone to microscopic crazing of the resin. This may be due in part to differential thermal co-efficients of expansion of the resin and glass, but appears also to be due to some extent to brittleness and shrinkage of the resin in drying out with further heating. These microscopic cracks subsequently allow ingress of moisture when damp conditions are encountered, causing further deterioration in insulating properties. In the case of such unmodified resins it is invariably found that all attempts to achieve removal of more water by extra drying—or heat-treatment—before pressing result in too much loss of flow, preventing good consolidation.

105 As already mentioned above, the modified resins used according to the present invention allow extensive pre-drying without such loss of flow and thereby overcome the aforesaid disadvantages and defects.

110 The following examples are given for the purpose of illustrating the invention. The "parts" mentioned are parts by weight.

EXAMPLE 1

115 To a slurry of 504 parts of finely ground melamine (4 mols), 490 parts of com-

mercial formalin containing 180 parts CH_2O (6 mols), and 374 parts of water, was added 137 parts of commercial Polyethylene Glycol 1500 together with 1.5 parts triethylamine as condensation agent. The mixture was heated rapidly to boiling point under a reflux condenser, yielding in about 10 to 15 minutes a clear solution which was then further condensed by boiling for a total of about $1\frac{1}{2}$ hours until a test sample of the solution cooled to 20° C . would just tolerate dilution with 2 volumes of water at 20° C . per volume of resin solution without causing precipitation of resin, whereupon the charge was rapidly cooled. A moderately viscous clear resin solution of good storage stability was obtained. 5

Closely-woven square-weave electrical-grade glass fabric approximately .005" thickness, flame cleaned at 450° — 500° C . for removal of organic sizing, was impregnated with said resin solution and drawn over rollers to ensure even coating and removal of excess resin solution. The conditions were adjusted so that after drying (about to be mentioned) of the impregnated fabric the material contained approximately 56.5% by weight of glass and 43.5% plasticised resin. From the impregnating bath the material was fed to a well-ventilated hot air oven with a residence time of about 10 minutes at 90° C . in the drying zone, followed by further heat treatment for 20 minutes at 120° C . for partial pre-cure of the resin. 10

Ten plies of this heat-treated resin-loaded fabric were assembled in a pack and hot-pressed between steel plates for 2 hours at 135° C . under an applied pressure of 1000 lbs per square inch on the pack, which was then cooled under pressure. Power factor tests of 15 this material were made according to the method of test described in B.S.S. 1137, and recorded .020 at 20° C . and 0.213 at 90° C . A test piece of the laminate was baked for 30 minutes at 100° C . in an air-oven, cooled, 20 stained with ink and examined under the microscope for crazing. No more than a few minute surface cracks were detected.

EXAMPLE 2

A commercial 1/1.5 mol ratio melamine-formaldehyde laminating resin, in spray-dried powder resin form, was dissolved at 50% concentration in water at 50° — 60° C . To 1000 g. lots of the solution were added respectively:— 25

(a) 100 gm. commercial Polyethylene Glycol 4000.
(b) 100 gm. commercial Polyethylene Glycol 6000, and the solutions cooled to room temperature. 30

Heat-cleaned glass fabric, as used in Example 1, was impregnated with solution (a) to give after drying a glass content of 56%. The drying was for about 10 minutes at 90° C . and this was followed by further

heat-treatment for 20 minutes at 110 — 112° C . in the air-oven. Ten plies of the heat-treated fabric were assembled and hot pressed for 3 hours at 125° C . and 1000 lbs per square inch pressure. 35

56% glass-content stock impregnated with solution (b) was similarly dried and heat-treated. 10-ply laminates thereof were cured during $2\frac{1}{2}$ hours at 125° C . under 1000 lbs, p.s.i. pressure. 40

Power-factor results of these laminates were as follows:—

(a) .022 at 20° C ; 0.17 at 90° C .
(b) .019 at 20° C ; 0.18 at 90° C . 45

EXAMPLE 3

Heat-cleaned glass fabric, as used in the foregoing examples, was impregnated with a solution comprising:—

100 parts commercial 1/1.5 mol ratio melamine-formaldehyde spray-dried powder laminating resin; 100 parts water; 15 parts commercial Polyethylene Glycol 1000; giving after drying approximately 56% glass-content stock. 50

The material was dried for 10 minutes at 90° C . and then heat-treated for 50 minutes at 100° — 105° C . in an air oven. 10-ply laminates for the heat treated material were pressede 2 hours at 125° C . under a pressure of 1000 lbs per square inch. Power factor results of the cured laminates were as follows:— 55

0.11 at 20° C ; 0.26 at 90° C . 60

EXAMPLE 4

Heat-cleaned glass fabric, as used in previous examples was impregnated with a solution comprising:—

100 parts commercial 1/2 mol ratio melamine-formaldehyde spray-dried powder laminating resin; 100 parts water; 20 parts commercial Polyethylene Glycol 4000, giving after drying 56% glass content stock. 65

The material was dried for 10 minutes at 90° C . and then heat treated for 12 minutes at 110 — 112° C . in the air oven. 10-ply laminates of the heat-treated material were cured during 3 hours at 125° C . under 1000 lbs per square inch pressure. 70

Power factor results of the cured laminates were as follows:—

0.028 at 20° C ; 0.532 at 90° C . 75

COMPARISON EXAMPLE

For comparison with the foregoing examples heat-cleaned glass fabric as used in said examples was impregnated with a 50% aqueous solution of the commercial 1/2 mol ratio melamine-formaldehyde spray-dried powder laminating resin to give 55%—56% glass content after drying. The material was dried for 10 minutes at 90° C . and in further experiments 15—20 minutes at 80° C . in an air-oven. Further drying or heat treatment 80

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of these material's led in all cases to loss of flow and insufficient fusibility to give good bonding in subsequent hot-pressing. 10-ply laminates were pressed, under a pressure of 1000 lbs per square inch, from the above material, having been cautiously dried as described, and cured for 2 hours at 125° C. Power factor results of cured laminates were of the order of 0.2—0.3 at 20° C. and greater than 1 at 90° C.

Test pieces of these laminates when baked for 30 minutes at 100° C. in the air-oven, cooled and stained with ink, showed very bad crazing of the material.

WHAT WE CLAIM IS:—

- Thermosetting compositions comprising aminotriazine-aldehyde resins modified by the incorporation of one or more polyethylene glycols of the general formula:
$$\text{HO}(\text{CH}_2\text{CH}(\text{O}(\text{CH}_2\text{CH}_2)_n\text{OH})$$

wherein n is 15 to 170, the ratio of aldehyde radicals to amino radicals in said resins being 0.43 to 2—CHO radicals per —NH₂ radical.

- Thermosetting compositions according to Claim 1, wherein the aminotriazine is melamine.
- Thermosetting compositions according to Claim 1, wherein the aminotriazine is aniline, melam or benzoguanamine in addition to, or instead of, melamine.
- Thermosetting compositions according to any of the preceding claims, wherein the aldehyde is formaldehyde.
- Thermosetting compositions according to Claims 2 and 4, wherein the mol ratio of formaldehyde to melamine ranges from 1.5:1 to 3:1.
- Thermosetting compositions according to any of the preceding claims, wherein the polyethylene glycol used is any of those hereinbefore specifically described.
- Thermosetting compositions according to any of the preceding claims, wherein the amount of polyethylene glycol used is from 2—30% by weight calculated on the weight of aminotriazine-aldehyde resin or aminotriazine-aldehyde resin-forming agents used.
- Thermosetting compositions substantially as hereinbefore described.
- Thermosetting compositions substantially as described in any of the examples.
- Process for the production of thermosetting compositions according to any of the Claims 1 to 9, characterised in that the polyethylene glycol is added to the reagents in the initial condensation process.
- Process for the production of thermosetting compositions according to any of Claims 1 to 9, characterised in that the polyethylene glycol is added to a solution or dispersion of the pre-condensed resin composition.
- Process for the production of thermosetting compositions according to any of

Claims 1 to 9, characterised in that the polyethylene glycol is added after partial condensation of the initial condensation reagents.

13. Process according to Claim 11 or 12, wherein the modified resin composition is subsequently dried and heat-treated.

14. Process for the production of thermosetting compositions according to any of Claims 1 to 9, characterised in that the resin is alkylated or partially alkylated by the addition of one or more alcohols containing 1—3 carbon atoms to the initial condensation reagents or after partial condensation has taken place.

15. Process according to Claim 14, wherein the alcohols containing 1—3 carbon atoms are monohydric alcohols.

16. Process according to Claim 15, wherein the monohydric alcohols are methanol or ethanol.

17. Process according to any of Claims 14 to 16, wherein the alcohols are added at the same time as the polyethylene glycol.

18. Process for the production of thermosetting compositions substantially as hereinbefore described and with reference to any of the specific examples.

19. Thermosetting compositions whenever prepared by the process according to any of Claims 10 to 18.

20. Process for the production of glass fabric laminates for electrical insulation, characterised in that an electrical-grade glass fabric is impregnated with an aqueous solution of a thermosetting composition according to any one of Claims 1 to 9, the thus treated fabric being subsequently heated in a current of hot air until the free water is evaporated and until the resin has been advanced in condensation by partial precure, resulting in some further degree of dehydration, the thus obtained resin-bonded fabric then being cut into sheets and a plurality of the plies being heated and cured in a hot-press.

21. Modification of the process according to Claim 20, wherein the resin is modified on the glass fabric, in that the glass fabric is treated with an aqueous solution of the aminotriazine-aldehyde resin and the polyethylene glycol.

22. Process for the production of resin-bonded glass fabric laminates, substantially as hereinbefore described and with reference to any of Examples 1 to 4.

23. Resin-bonded glass fabric laminates whenever produced by the process according to any one of Claims 20 to 22.

24. Electrical insulated materials, whenever made from resin-bonded glass fabric materials according to any of Claims 20 to 23.

25. Laminated materials which contain thermosetting compositions according to any of Claims 1 to 9.

26. Moulded and heat-pressed products, whenever prepared from thermosetting com-

positions according to any one of Claims 1 to 9.

27. Moulding powders whenever prepared from mineral-filled thermosetting compositions according to any of Claims 1 to 9.

28. Moulded products whenever made

from moulding powder according to Claim 27.

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PROVISIONAL SPECIFICATION

Improvements in and relating to Modified Aminotriazine-Formaldehyde Resin Compositions

We, BRITISH INDUSTRIES PLASTICS LIMITED, a Company organised under the Laws of Great Britain, Haymarket House, 28, Haymarket, London, S.W.1, do hereby declare this invention to be described in the following statement:—

15 This invention relates to thermosetting compositions and more particularly to the manufacture of improved thermosetting compositions comprising aminotriazine-aldehyde resins, especially such compositions as are used as thermosetting moulding and laminating compositions, and mouldings and laminates produced therefrom.

According to the invention thermosetting compositions comprising amino-triazine-aldehyde resins are modified to improve their plasticity or flow and fusibility characteristics under heat by the incorporation in the composition of one or more polyethylene glycols of the typical composition

30 $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot (\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_n \cdot \text{OH}$, and of molecular weight within the range 722 to 7542, i.e. where $n=15$ to 170. Such compositions containing a partially-condensed aminotriazine-aldehyde resin and a suitable

35 polyethylene glycol are particularly advantageous, and it is possible, according to the invention, to provide cured moulded and laminated articles by forming such a partially-condensed composition and then curing.

40 In the manufacture of modified or plasticised composition according to the invention, formaldehyde is the preferred aldehyde but other aldehydes, e.g. benzaldehyde, may be used as well, or instead, if desired.

45 The preferred aminotriazine is melamine, but related compounds such as ammeline, melam and benzoguanamine may be used as well, or instead, if desired. The ratio of aldehyde to aminotriazine may range from about 0.5 to

50 2—CHO radicals per —NH₂ group of the aminotriazine employed, corresponding in the case of melamine formaldehyde resins to molecular proportions of 1.3:1 to 6:1 of formaldehyde to melamine. In the case of

55 melamine a mol ratio of 1.5:1 to 3:1 is preferred. It will be understood that suitable resin-forming reagents may be employed as well as, or instead of the resins themselves.

60 The preferred proportions of polyethylene glycol will normally range for most purposes from 2% to 30% by weight on

the weight of aminotriazine-aldehyde resin or resin-forming reagents used, but the invention is not restricted or limited to these proportions. The polyethylene glycols may be added if desired as reagents or modifiers in the initial condensation process to form the aminotriazine-aldehyde resin, or at any convenient stage after partial condensation, and submitted thereafter to further condensation or final curing, whenever desired. Catalysts and/or initiation agents, and other additives may be added if desired.

65 Suitable polyethylene glycols over the desired range of molecular weights are available commercially. Minor amounts of higher or lower molecular weight glycols may be present as well, if desired, but in general it is found that resin-compatibility diminishes progressively with increasing molecular weight; and water solubility, which tends to impair water-resistance of the cured resin products, increases with lower molecular weight, thus limiting the usefulness of materials outside the above defined range.

70 Suitable materials are "Carbowax" (Registered Trade Mark), Polyethylene Glycols 1000 (mol wt. range 950—1050); 1540 (mol wt. range 1300—1600); 4000 (mol wt. range 3000—3700); and from another source (Oxitane Ltd.) Technical grades described as 800 (mol wt. range 760—840); 1000 (mol. wt range 950—1050); 1500 (mol wt. range 1300—1600); 4000 (mol wt. range 3000—4000); 6000 (mol. wt. range 5000—7500).

75 When present during the condensation reactions, the polyethylene glycols appear to react as resin-modifiers and contribute appreciably to improved storage stability of the aqueous resin compositions. They may be added, alternatively, to pre-condensed resin composition solutions or dispersions which may then be dried and heat-treated, or if desired solid fusible resin compositions or partially-condensed dry powder resin compositions may be blended with the polyglycols and heat-treated, to advance the degree of polymerisation while conserving adequate fusibility of the products.

80 It is possible thereby to obtain partially-cured resin products which even after very thorough pre-drying or pre-cure still retain adequate resin-flow and fusibility for hot-

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press moulding and laminating applications. The resultant cured products accordingly have much improved dimensional stability (mould-shrinkage and after shrinkage are reduced), better resistance to crazing under dry heat and much superior electrical properties.

Hot-pressed products of the invention generally have improved plasticity and flexibility, especially while hot or when re-heated. Machining properties of products comprising cellulose or other organic fillers, especially hot punching and post-forming properties, are thereby improved.

The modified resins are especially valuable for the production of glass-fabric laminates for high-duty electrical insulation, where previously no really suitable resin plasticisers or modifiers for aqueous systems of amino-triazine-aldehyde resins have been found to give all the requirements of high dielectric strength, good water-resistance, low power factor at 90° C., good resistance to tracking and arcing, and non-inflammability of the finished products.

Melamine-resin bonded glass fabric laminates for electrical insulation are normally made by impregnating electrical-grade glass fabric with an aqueous solution of the resin and drying the stock in a current of hot air until all the free water is evaporated and the resin has been advanced in condensation to some extent by partial pre-cure, resulting in some further degree of dehydration. The resin-loaded fabric is then cut into sheets and a plurality of these plies is then consolidated and cured in a hot-press. For good consolidation it is essential that the resin shall have adequate flow and fusibility to allow complete expression of air so that all voids are filled with resin and so eliminated; and for good electrical insulation values it appears essential that the residual hydroxyl-content, or methylol groups, of the resin shall be reduced by drying and pre-cure to the lowest possible value consistent with retention of sufficient resin fusibility, so that further elimination of water from the resin during cure in the hot press is also reduced to a minimum. With unmodified resins obtained by the aqueous condensation of melamine and formaldehyde it is found, because of these considerations, that although laminates of high dielectric strength can be made without any great difficulty, the residual traces of water of condensation liberated during cure of the resin in hot-pressing are contained in the products, and their effect is to cause a very considerable worsening of the power factor of the material in use at elevated temperatures. A further defect is that under dry heat such products are found to be very prone to microscopic crazing of the resin. This may be due in part to differential thermal co-efficients of expansion of the

resin and glass, but appears also to be due to some extent to brittleness and shrinkage of the resin in drying out with further heating. These microscopic cracks subsequently allow ingress of moisture when damp conditions are encountered, causing further deterioration in insulating properties. In the case of such unmodified resins it is invariably found that all attempts to achieve removal of more water by extra drying—or heat-treatment—before pressing result in too much loss of flow, preventing good consolidation.

As already mentioned above, the modified resins used according to the present invention allow extensive predrying without such loss of flow and thereby overcome the aforesaid disadvantages and defects.

The following examples are given for the purpose of illustrating the invention. The "parts" mentioned are parts by weight.

EXAMPLE 1

To a slurry of 504 parts of finely ground melamine (4 mols), 490 parts of commercial formalin containing 180 parts CH_2O (6 mols.), and 374 parts of water, was added 137 parts of commercial Polyethylene Glycol 1500 together with 1.5 parts triethylamine as condensation agent. The mixture was heated rapidly to boiling point under a reflux condenser, yielding in about 10 to 15 minutes a clear solution which was then further condensed by boiling for a total of about 1½ hours until a test sample of the solution cooled to 20° C. would just tolerate dilution with 2 volumes of water at 20° C. per volume of resin solution without causing precipitation of resin, whereupon the charge was rapidly cooled. A moderately viscous clear resin solution of good storage stability was obtained.

Closely-woven square-weave electrical-grade glass fabric approximately .005" thickness, flame cleaned at 450°—500° C. for removal of organic sizing, was impregnated with said resin solution and drawn over rollers to ensure even coating and removal of excess resin solution. The conditions were adjusted so that after drying (about to be mentioned) of the impregnated fabric the material contained approximately 56.5% by weight of glass and 43.5% plasticised resin. From the impregnated bath the material was fed to a well-ventilated hot air oven with a residence time of about 10 minutes at 90° C. in the drying zone, followed by further heat treatment for 20 minutes at 120° C. for partial pre-cure of the resin.

Ten plies of this heat-treated resin-loaded fabric were assembled in a pack and hot-pressed between steel plates for 2 hours at 135° C. under an applied pressure of 1000 lbs. per square inch on the pack, which was then cooled under pressure. Power factor

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tests of this material were made according to the method of test described in B.S.S. 1137, and recorded .020 at 20° C. and 0.213 at 90° C.

5 A test piece of the laminate was baked for 30 minutes at 100° C. in an air-oven, cooled, strained with ink and examined under the microscope for crazing. No more than a few minute surface cracks were detected.

10 EXAMPLE 2

A commercial 1/1.5 mol. ratio melamine-formaldehyde laminating resin, in spray-dried powder resin form, was dissolved at 50% concentration in water at 50°—60° C. To 1000 gm. lost of the solution were added respectively:—

(a) 100 gm. commercial Polyethylene Glycol 4000.

20 (b) 100 gm. commercial Polyethylene Glycol 6000, and the solutions cooled to room temperature.

Heat-cleaned glass fabric, as used in Example 1, was impregnated with solutions

25 (a) to give after drying a glass content of 56%. The drying was for about 10 minutes at 90° C. and this was followed by further heat-treatment for 20 minutes at 110°—112° C. in the air-oven. Ten plies of the heat-treated fabric were assembled and hot pressed for 3 hours at 125° C. and 1000 lbs. per square inch pressure.

50 56% glass-content stock impregnated with solution (b) was similarly dried and heat-treated.

35 10-ply laminates thereof were cured during 2½ hours at 125° C. under 1000 lbs. p.s.i. pressure.

Power-factor results of these laminates were as follows:—

(a) .022 at 20° C. 0.17 at 90° C.

40 (b) .019 at 20° C. 0.18 at 90° C.

EXAMPLE 3

Heat-cleaned glass fabric, as used in the foregoing examples, was impregnated with a solution comprising:—

45 100 parts commercial 1/1.5 mol. ratio melamine-formaldehyde spray-dried powder laminating resin;

100 parts water;

50 15 parts commercial Polyethylene Glycol 1000, giving after drying approximately 56% glass-content stock. The material was dried for 10 minutes at 90° C. and then heat-treated for 50 minutes at 100°—105° C. in an air oven. 10-ply laminates of the heat treated material were pressed 2 hours at 125°

C. under a pressure of 1000 lbs. per square inch. Power factor results of the cured laminates were as follows:—
.011 at 20° C. 0.26 at 90° C.

EXAMPLE 4

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Heat-cleaned glass fabric, as used in previous examples was impregnated with a solution comprising:—

100 parts commercial 1/2 mol. ratio melamine-formaldehyde spray-dried powder laminating resin; 65

100 parts water;

20 parts commercial Polyethylene Glycol 4000, giving after drying 56% glass content stock. 70

The material was dried for 10 minutes at 90° C. and then heat treated for 12 minutes at 110°—112° C. in the air oven. 10-ply laminates of the heat-treated material were cured during 3 hours at 125° C. under 1000 lbs. per square inch pressure. 75

Power factor results of the cured laminates were as follows:—

0.028 at 20° C. 0.532 at 90° C.

COMPARISON EXAMPLE

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For comparison with the foregoing examples heat-cleaned glass fabric as used in said examples was impregnated with a 50% aqueous solution of the commercial 1/2 mol. ratio melamine-formaldehyde spray-dried powder laminating resin to give 55%—56% glass content after drying. The material was dried for 10 minutes at 90° C., and in further experiments 15—20 minutes at 80° C., in an air-oven. Further drying or heat treatment of these materials led in all cases to loss of flow and insufficient fusibility to give good bonding in subsequently hot-pressing. 10-ply laminates were pressed under a pressure of 1000 lbs. per square inch, from the above material, having been cautiously dried as described, and cured for 2 hours at 125° C. 85

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Power factor results of cured laminates were of the order of 0.2—0.3 at 20° C. and greater than 1 at 90° C. 95

Test pieces of these laminates when baked for 30 minutes at 100° C. in the air-oven, cooled and strained with ink, showed very bad crazing of the material. 100 105

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